

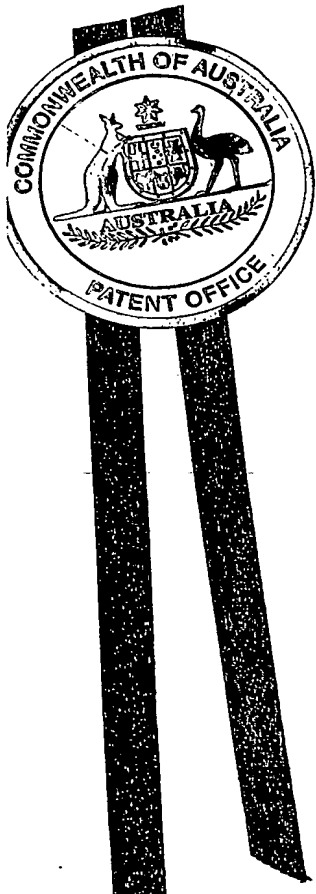
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I, LEANNE MYNOTT, MANAGER EXAMINATION SUPPORT AND SALES hereby certify that annexed is a true copy of the Provisional specification in connection with Application No. 2004905629 for a patent by MT ASPIRING GEOCHEMISTRY CONSULTANTS PTY LTD as filed on 29 September 2004.



WITNESS my hand this
Fourteenth day of January 2005

A handwritten signature in black ink, appearing to be 'LM' or similar initials.

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PROVISIONAL SPECIFICATION FOR THE INVENTION ENTITLED:

Cementitious Composition and Method of Manufacture Thereof

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This invention is best described in the following statement:

Cementitious Composition and Method of Manufacture Thereof

Technical Field of the Invention

The present invention relates to cementitious compositions. More particularly, the invention relates to cementitious compositions that can be produced and applied using conventional pouring, pumping, grouting and shotcreting methods, and that are useful for application as acid resistant cementitious compositions, sulfate resistant cementitious compositions, saline brine resistant cementitious compositions, fine-grained surface textured cementitious compositions, aerated or blown cementitious compositions, terracotta cementitious compositions, and the like. The invention also relates to a process for the manufacture of such compositions.

Background of the Invention

At their most basic level, concretes consist of sand, gravel (or aggregate) and cement that are combined with water to promote a tobermorite gel that binds the sand and gravel (or aggregate) as a solid mass, by converting oxides into aluminates and silicates. For ordinary Portland cement (OPC), the four principle components of cementation are tri-calcium silicate (C3S), di-calcium silicate (C2S), tri-calcium aluminate (C3A) and tetra-calcium aluminoferrite (C4AF). High alumina cements are also used to provide superior resistance to saline waters and high temperatures, but these generally have lower strengths and are more expensive.

Table: 1 Some common cementitious compositions

Sand	Gravel	Cement	Other*	Purpose
6	0	1	0-1	Mortar
4	3	1	0-1	Fill Concrete
3	4	1	0-1	Coarse Fill Concrete
5	2	1	0-1	General Purpose Concrete
2	3	1	0-1	Structural Concrete

*other components may include fly ash, silica fume, plasticizer and reinforcing.

Red mud is a residue that forms as a by-product when bauxite is converted, through the Bayer Process, into aluminium hydroxide and alumina. It contains a wide range of compounds originating from the unwanted constituents of bauxite, including iron oxyhydroxides (which cause its colour to be red), aluminium hydroxides, other metals,

silica and silicates. Because caustic soda is used in the Bayer Process to dissolve the alumina part of bauxite, red mud is very caustic. It usually has a pH in excess of 13. For that reason, and also for cost reasons, the maximum amount of caustic is usually recovered from red mud before it is discarded, usually in large holding dams.

5 Large quantities of red mud are produced annually by bauxite-refineries in Australia and other countries, and because of the environmental problems that could potentially be caused by the caustic red mud, particularly where it has been dumped over a long period of time, economically sustainable and environmentally acceptable methods of disposal thereof are in great demand.

10 Various attempts have been made to utilize red mud in cementitious compositions. In this regard, Singh, M, reviewed the literature in Chapter I of his MTech dissertation entitled: *Studies on the Preparation of Stabilized Blocks and Special Cements from Hindalco's Uncausticized Mud and Fly Ash*, Department of Chemical Engineering & Technology, Institute of Technology, Banaras Hindu University, Varanasi, India (May 15 1995). However, none of the publications reviewed in this dissertation disclosed the cementitious compositions of the present invention or processes of making them.

Bricks containing red mud, cement and sand have been made in Jamaica. The bricks were found to have a compressive strength of about 4.7 MPa.

20 French patent publication No 2 760 003 discloses an iron-rich cement clinker containing red mud and limestone or other calcium oxide containing material. The clinker was fired in a kiln at a temperature of from 1175°C to 1250°C. Washed and unwashed red mud was used. This document also discloses an hydraulic cement that was obtained from the aforementioned clinker. It furthermore discloses the production of hydraulic cements and mortars from a red mud based cement clinker mixed with lime-containing material 25 and additional red mud. Apart from washing with water and heating to a temperature exceeding 1175°C, at which certain constituents of red mud will have decomposed, this document does not disclose any further processing of the red mud before it is incorporated in the cementitious compositions.

30 US Patent No. 5,456,553 describes the use of red mud combined with iron oxide powder and lime as a reinforcing agent for soil. It does not disclose the production of a cementitious composition nor of concrete.

US Patent No. 5,931,772 describes the production of compositions using dewatered, dried and sieved red mud combined with a waste material, followed by mixing with a pozzolanic material (cement, flyash or lime). This patent describes the treatment and encapsulation of a waste product as a relatively chemically inactive solid waste for disposal as landfill. The red mud used was not neutralized.

US Patent No. 3,989,513 describes the mixing of red mud with calcium oxide materials and reducing agents for the purpose of smelting iron ore at high temperatures. This patent does not disclose the use of red mud in cementitious compositions.

The Canadian Building Digest (<http://irc.nrc-cnrc.gc.ca/cbd/cbd215e.html>) suggests the use of vitrified red mud as a concrete aggregate. Vitrified red mud differs from red mud as vitrified red mud is chemically inactive. Vitrified red mud is used as a filling agent only. Vitrification removes the geochemical reactivity of red mud.

The International Research Development Centre (1992) http://web.idrc.ca/en/ev-2691-201-1-do_TOPIC.html suggested the mixing of red mud with other waste products, including flyash, to create construction bricks. Glanville, J.I. (1991). *Bauxite waste bricks (Jamaica): Evaluation Report*, June 1991. IDRC, Ottawa, evaluated bricks made of red mud and other waste products and indicated that the high sodium content caused salt leaching and salt efflorescence, which weakened the structures built using the red mud bricks. These publications did not consider the reduction in sodicity or the salt content of red mud used in brick construction.

Wagh, A.S., & Douse, V.E. (1991). *Silicate bonded unsintered ceramic of Bayer process waste*, Journal of Materials Research. Pittsburgh, Pa.: 6(5) 1095-1102 described the use of a silicate bonded ceramic made of Bayer process waste, as a ceramic material. This publication did not disclose the use of cement as a pozzolanic material in a composition together with red mud, or the use of red mud as a construction material, or the use of neutralised red mud with reduced sodicity.

Summary of the Invention

According to a first aspect of the invention, there is provided a cementitious composition comprising partially neutralised red mud and cement, wherein the partially neutralised red mud has been pre-treated by contacting it with water having a total hardness supplied by calcium, magnesium or a combination thereof, of at least 3.5 millimoles per litre calcium carbonate equivalent.

In the pre-treatment of the red mud, its pH may be reduced to a value of at most about 10.5 and at least about 8.2. The pH of the red mud may conveniently be reduced to anywhere within the range of 8.2 to 10.5. It is preferably reduced to a value as low as possible within the aforementioned range. The pH may be reduced to about 8.5 - 10, or
5 alternatively to about 8.5 - 9.5, or alternatively to about 8.5 - 9.5, or as another alternative, to about 9 - 10, or as a further alternative to about 9.5 - 10, or from about 9 - about 9.5.

According to a second aspect of the invention, there is provided a process for the manufacture of a cementitious composition comprising

- 10 - (a) contacting red mud recovered from the Bayer Process with water having a total hardness supplied by calcium, magnesium or a combination thereof, of at least 3.5 millimoles per litre calcium carbonate equivalent, so as to obtain a partially neutralised red mud; and
- 15 - (b) mixing the partially neutralised red mud with cement so as to obtain the cementitious composition.

In step (a), the pH of the red mud may be reduced to a value of at most about 10.5 and at least about 8.2. The pH of the red mud may conveniently be reduced to anywhere within the range of 8.2 to 10.5. It is preferably reduced to a value as low as possible within the aforementioned range. The pH may be reduced to about 8.5 - 10, alternatively
20 to about 8.5 - 9.5, as another alternative, to about 9 - 10, as a further alternative to about 9.5 - 10, or from about 9 - about 9.5.

The process according to the second aspect of the invention may include a step (a1), after step (a) and before step (b), in which the partially neutralised red mud is dried to obtain a dry solid material.

25 The process according to the second aspect of the invention may include a further step (a2), after step (a1) and before step (b), in which the dry solid material of step (a1) is comminuted so as to obtain a partially neutralised dry, comminuted red mud.

The cement may be present in the composition in a concentration of from about 1 wt% to about 99 wt% and the partially neutralised red mud may be present in the
30 composition in a concentration of from about 99 wt% to about 1 wt%.

The comminution in step (c) may be performed by crushing and/or pulverising. It may be performed by any crusher and/or pulveriser, which may be a cone crusher, a rod mill, a ball mill, a jaw crusher or an orbital crusher.

The invention also extends to a cementitious composition made by the process according to the invention.

Optionally, the process according to the invention includes a step, after step (a) and before step (b), of contacting the red mud with, or a partially reduced red mud with, an acid so as to perform part of the overall lowering of the pH of the red mud to at most about 10.5 and at least about 8.2.

As a further option, the process may include a step of separating a liquid phase from the red mud, or the partially reduced pH red mud, after step (a) and before step (b).

The water used in the first and second aspects for the pre-treatment of the partially neutralised red mud, in step (a) of the process according to the invention, should have a total hardness supplied by calcium plus magnesium of more than 3.5 millimoles calcium carbonate equivalent per litre. However, in order to reach the pH of less than 10.5, the water preferably has a total hardness supplied by calcium plus magnesium in excess of about 5 millimoles per litre calcium carbonate equivalent, more preferably, in excess of 10 millimoles per litre calcium carbonate equivalent, even more preferably, in excess of about 15 millimoles per litre calcium carbonate equivalent. The water conveniently has a base amount and a treatment amount of at least one of calcium and magnesium. The base amount for calcium is about 150 mg/L (1.5 millimoles per litre calcium carbonate equivalent) and the base amount for magnesium is about 250 mg/L (2.5 millimoles calcium carbonate equivalent). Although satisfactory results have been obtained with brine containing about 200 to about 300 mg/L calcium and from about 300 to about 750 mg/L magnesium, it was found that, for the treatment to work efficiently, concentrations exceeding 300 mg/L calcium and 750 mg/L magnesium are preferred. The concentrations that are best for any particular set of circumstances depend on the solubilities of various compounds that may be formed in the solution, the temperature of the solution and the service and environmental conditions under which the cementitious composition is to be used.

The water used for the pre-treatment of the partially neutralised red mud in step (a) thus preferably contains a significantly higher concentration of calcium and/or magnesium than is available in ordinary tap water. Regulations governing tap or drinking

water quality usually include guidelines based on hardness (which is usually expressed as CaCO_3 equivalent). The total hardness (Ca hardness plus Mg hardness) of a drinking water should be less than 500 mg/L which is equivalent to less than about 5 millimoles per litre. Therefore, the combined concentrations of Ca and Mg should be less than about 5 millimoles per litre, which is very low compared to the Ca and Mg concentrations used for the neutralization or partial neutralization of red mud in step (a) of the process according to the invention. When water is hard, soaps and other detergents will not foam. Instead, a scum is formed on the water surface. A range of criteria for hardness may be as follows:

10	Soft water:	0-59 mg/L (0-0.59 mM)
	Moderately soft water:	60-119 mg/L (0.6-1.19 mM)
	Hard water:	120-179 mg/L (1.2-1.79 mM)
	Very Hard water:	180-240 mg/L (1.8-2.4 mM)
	Extremely Hard water:	>400 mg/L (>4 mM)

15 Water having a hardness of less than 60 mg/L has an increased corrosion potential on iron and steel fittings, pumps and pipes, whereas water having a hardness of more than 350 mg/L has an increased potential for fouling and scale formation. Consequently, to avoid the abovementioned undesirable effects, drinking water should have a total hardness not exceeding 350 mg/L (which is equivalent to about 3.5 millimoles of Ca plus Mg). A good quality drinking water preferably has a total hardness in the range of 60-180 mg/L (which is equivalent to about 0.6-1.8 millimoles of Ca plus Mg).

In step (a) of the process according to this aspect of the invention, the pH of the red mud is conveniently reduced to anywhere within the range of 8.2 to 10.5. The pH is conveniently reduced to about 8.5 - 10, alternatively to about 8.5 - 9.5, or alternatively to 25 about 8.5 - 9, or as another alternative to about 9 - 10, or as a further alternative to about 9.5 - 10, or from about 9 - about 9.5.

In step (a) of the process according to this aspect of the invention, the total alkalinity, expressed as calcium carbonate alkalinity, of the red mud may be reduced to about 200 mg/L - 1000 mg/L, alternatively to about 200 mg/L - 900 mg/L, alternatively to 30 about 200 mg/L - 800 mg/L, alternatively to about 200 mg/L - 700 mg/L, alternatively to about 200 mg/L - 600 mg/L, alternatively to about 200 mg/L - 500 mg/L, alternatively to about 200 mg/L - 400 mg/L, alternatively to about 200 mg/L - 300 mg/L, alternatively to about 300 mg/L - 1000 mg/L, alternatively to about 400 mg/L - 1000 mg/L, alternatively

to about 500 mg/L - 1000 mg/L, alternatively to about 600 mg/L - 1000 mg/L, alternatively to about 700 mg/L - 1000 mg/L, alternatively to about 800 mg/L - 1000 mg/L, alternatively to about 900 mg/L - 1000 mg/L, preferably less than 300 mg/L.

In step (a) of this process, the pH is conveniently reduced to less than about 10.5, preferably to less than about 9.5, more preferably to less than about 9.0, and the total alkalinity, expressed as calcium carbonate equivalent alkalinity, is reduced to less than 300 mg/L and preferably reduced to less than 200 mg/L.

A preferred composition comprises from 50% to 95% by dry weight of partially neutralised red mud and from 5% to 50% by weight of cement. A more preferred composition comprises from 70% to 90% by dry weight of partially neutralised red mud and from 10% to 30% by dry weight of cement. A most preferred composition comprises from 80% to 85% by dry weight of the partially neutralised red mud and from 15% to 20% by weight of the cement.

In one embodiment of the invention, the composition comprises at least 30 wt% of partially neutralised red mud. In another embodiment, the composition comprises at least 50 wt % of partially neutralised red mud.

The inventors have found that cementitious compositions made with partially neutralised red mud maintain a high acid neutralising and metal binding capacity. These compositions are capable of treating acidity produced as a result of pyrite oxidation, or by any other means, and are sulfate resistant. The inventors also found that, up to certain limits, imposed by the demands of particular applications, partially neutralised red mud can act as a cement replacement that does not adversely affect the strength of the composition, and will adhere to steep rock faces so as to help stabilise them against potential rock falls. They further found that the composition according to the invention, when dry, does not produce an appreciable dust problem and is capable of being moulded into articles having very fine textural or surface detail.

The composition according to the invention may be used as a substitute for a conventional cementitious composition, without substantial reduction in strength.

The composition according to the present invention may be used to produce a castable material that has the ability to be moulded such that fine textural detail on the mould surface is transferred to and preserved on the mould surface.

In one embodiment of the invention, from 0.2 wt % to 3 wt% of the cement of a super-plasticizer for example MAPEI™ N10 and R14, MAPETAR™ or MAPEPLAST RMX may be added to the composition according to the present invention, to produce a shotcrete that has an enhanced acid neutralising capacity, that will trap heavy metals, and that is capable of being sprayed onto vertical walls.

In another embodiment of the invention, additional water and from 0.2 wt % to 3 wt% of the cement of a super-plasticizer for example MAPEI™ N10 and R14, MAPETAR™ or MAPEPLAST RMX may be added to the composition according to the present invention, to produce a grout that can be pressure injected into rock or soil materials to increase their strength and reduce their permeability and to neutralise any acidity and trap any trace metals that may be present in pore fluids.

In another embodiment of the invention, the composition according to the present invention is extruded into porous pellets that are subsequently cured and dried. The dried pellets may then be used for acidic water remediation. Such remediation may be performed in an underground water duct or aquifer or else in a treatment vessel.

The partially neutralised red mud may be prepared by at least partially reacting red mud from a bauxite refinery by the addition of calcium and/or magnesium ions in an aqueous solution, or by the addition of an acid; or by an injection of carbon dioxide or by adding a mineral such as gypsum, or by some combination of these procedures.

Alternatively, the partially neutralised red mud may be prepared by at least partially reacting red mud from a bauxite refinery with a material selected from the group consisting of a ferruginous residue recovered from titanium refining process, a ferruginous soil, a ferruginous rock material (such as fines produced as a by product of iron ore mining) or bauxite.

A partially neutralised red mud that works particularly well is available from Virotec International Pty Ltd of Sanctuary Cove, Queensland, Australia, under the trademark Bauxsol.

As described in International Patent Application No. PCT/AU03/00865, the contents of which are incorporated herein in their entirety, red mud from a bauxite refinery may be reacted with calcium and/or magnesium ions. Another way in which the

at least partially neutralised red mud may be prepared is by reacting red mud from a bauxite refinery with a sufficient quantity of seawater, preferably seawater concentrated by evaporation, conveniently by solar action, to decrease the reaction pH of the red mud to less than 10.5. For example, it has been found that if an untreated red mud has a pH of about 13.5 and an alkalinity of about 20,000 mg/L, the addition of about 5 volumes of world average seawater will reduce the pH to between 9.0 and 9.5 and the alkalinity to about 300 mg/L. International Patent Application No. PCT/AU03/00865 furthermore teaches that red mud from a bauxite refinery may be reacted with calcium and/or magnesium ions by mixing one part of the red mud with 5 parts by weight of water

containing a base amount and a treating amount of calcium ions and a base amount and a treating amount of magnesium ions, for a time sufficiently long to bring the reaction pH of the red mud to less than 10.5. The base amounts of calcium and magnesium ions are 8 millimoles and 12 millimoles, respectively, per litre of the total volume of the treating solution and the red mud. The treating amount of calcium ions is at least 25 millimoles per mole of total alkalinity of the red mud expressed as calcium carbonate equivalent alkalinity whilst the treating amount of magnesium ions is at least about 400 millimoles per mole of total alkalinity of the red mud expressed as calcium carbonate equivalent alkalinity. Suitable sources of calcium or magnesium ions include any soluble or partially soluble salts of calcium or magnesium, such as the chlorides, sulfates or nitrates of calcium and magnesium.

As described in International Patent Application No. PCT/AU03/00865, partially neutralised red mud may be in the form of a dry red solid that consists of a complex mixture of minerals.

The general composition of partially neutralised red mud depends on the composition of the bauxite ore, from which it derives, on operational procedures used at a refinery at which the bauxite is processed, as well as by how the red mud has been treated after production.

Neutralisation of raw red mud from a bauxite refinery is achieved when the addition of soluble Ca and Mg salts converts soluble hydroxides and carbonates into low solubility mineral precipitates McConchie, D., Clark, M.W., Fawkes, R., Hanahan, C. and Davies-McConchie, F., 2000. *The use of seawater-neutralised bauxite refinery residues in the management of acid sulfate soils, sulphidic mine tailings and acid mine drainage*. In: 3rd

Queensland Environment Conference, 1, pp. 201-208, Brisbane, Australia. This procedure lowers the basicity to a pH of about 9.0 and converts most of the soluble alkalinity into solid alkalinity. More specifically, hydroxyl ions in the red mud wastes are largely neutralised by reaction with magnesium in the seawater to form brucite
 5 [Mg₃(OH)₆] and hydrotalcite [Mg₆Al₂CO₃(OH)₁₆.4H₂O], but some are also consumed in the precipitation of additional boehmite [AlOOH] and gibbsite [Al(OH)₃] and some reacts with calcium in the seawater to form hydrocalumite [Ca₂Al(OH)₇.3H₂O] and p-aluminohydrocalcite [CaAl₂(CO₃)₂(OH)₄.3H₂O]. The average composition of partially neutralised red mud, using sea water concentrated by solar evaporation, is as follows:

10	iron oxy-hydroxide (hematite):	31.6%;
0	aluminium oxy-hydroxides (gibbsite):	17.9%;
	sodalite:	17.3%;
	quartz:	6.8%;
	cancrinite:	6.5%;
15	titanium oxides (anatase):	4.9%;
	calcium-alumino-hydroxides and hydroxy-carbonates (e.g. hydrocalumite):	4.5%;
	magnesium-alumino-hydroxides and hydroxy-carbonates (e.g. hydrotalcite):	3.8%;
	calcium carbonate:	2.3%;
	halite:	2.7%;
20	others (e.g. gypsum):	1.7%.

Partially neutralised red mud contains abundant Al, Fe, Mg, and Ca hydroxides and carbonates to provide either tobermorite gel constituents for the setting of concretes, or provide appropriate additives to induce early setting of the concrete. Conversely, increased gypsum content within partially neutralised red mud can retard setting rates.

25 Where red mud from a bauxite refinery has been partially neutralised using sea water, or evaporatively concentrated sea water, or other calcium- and magnesium-rich brines, or soluble calcium and magnesium salts, or some combination of these options, the partially neutralised red mud still has a high acid neutralising capacity (2.5 - 7.5 moles of acid per kg of partially neutralised red mud). It also has and a very high trace metal
 30 trapping capacity (greater than 1,000 milliequivalents of metal per kg of partially

neutralised red mud). It furthermore has a high capacity to trap and bind phosphates and some other chemical species. Partially neutralised red mud can be produced in various forms to suit individual applications (e.g. slurries, powders, pellets, etc.) but all have a near-neutral soil reaction pH (less than 10.5 and more typically between 8.2 and 8.6) despite their high acid neutralising capacity. The soil reaction pH of partially neutralised red mud is sufficiently close to neutral and its TCLP (Toxicity Characteristic Leaching Procedure) values are sufficiently low that it can be transported and used without the need to obtain special permits.

A particular benefit of using partially neutralised red mud in the compositions and methods of the invention is that the soluble salt concentrations, especially sodium concentrations, are substantially lower than those in untreated red mud. This effect can be particularly important where the salinity of treated waters to be discharged to environments that are sensitive to sodium or salinity increases, or where salinity of discharge waters to be used as irrigation waters may adversely affect plant growth, have a lower potential impact. Furthermore, decreased soluble salt concentrations contribute to increased final strength of cementitious compositions in accordance with the invention.

Concrete strength is dominated by the formation of tobermorite gel formation. Most typically, tobermorite gel is produced in the setting of an hydraulic cement. Hydraulic cements include ordinary Portland cement, high early strength Portland cement, low heat Portland cement, sulfate resisting Portland cement, high alumina cement and other commercially available cementing agents. In this specification, the expression "cement" is to be understood as including the aforementioned examples of hydraulic cement.

Within a tobermorite gel, four main constituents are usually present: tricalcium silicate (C3S), dicalcium silicate (C2S) tricalcium aluminate (C3A) and tetracalcium alumino-ferrate (C4AlFe).

When red mud is partially neutralised (either by brine addition or by seawater or concentrated sea water addition, with or without supplementation by soluble magnesium and calcium salts), the alkalinity of the red mud is converted from a soluble form which is predominantly sodium carbonate and sodium-hydroxide into an insoluble form which is precipitated as solids as a series of alumino-hydroxy carbonates. The excess sodium is drained from the system with the remaining brine. The alumino-hydroxy carbonates act as a pH buffering system against acid attack. However, they also provide additional

pozzolanic material such that cement, including OPC, may be partly substituted by partially neutralised red mud in a cementitious composition, without a significant reduction in strength of the composition.

Un-neutralised red mud (dried or wet) has a high Na content that is detrimental to the strength development of cementitious compositions. The monovalent alkali metals (Na and K) in such cementitious compositions interact with the tobermorite gel to produce Alkali-Aggregate Reactions, Alkali-Carbonate Reactions and Alkali-Silica Reactions (see www.pavement.com).

An Alkali-Aggregate Reaction is a chemical reaction in mortar or concrete between an alkali metal (sodium or potassium) released from Portland cement or from other sources, and certain compounds present in the aggregates. Under certain conditions, harmful expansion of the concrete or mortar may be caused by these reactions, which are detrimental to strength development.

An Alkali-Carbonate Reaction is a reaction between an alkali metal (sodium or potassium) and certain carbonate rocks, particularly calcite, dolomite and dolomitic limestones, present in some aggregates. The products of the reaction may also cause abnormal expansion and cracking of concrete in service.

An Alkali-Silica Reaction is a reaction between an alkali metal (sodium or potassium) and certain siliceous rocks or minerals, such as opaline silica, chert, chalcedony, flint strained quartz and acidic volcanic glass, present in some aggregates. The products of this reaction may also cause abnormal expansion and cracking of concrete in service.

The expansion and cracking induced by a high sodium content in cementitious composition could be exacerbated by the formation of silica gels, which can also lead to decreased final strength and a shortened service life.

Water washed (to remove a high proportion of the hydroxide red muds, although having a much reduced sodium content, also have little acid neutralising capacity. They are undesirable in cementitious compositions according to the invention because they do not contribute sufficiently to the acid neutralizing capacity of the cementitious compositions according to the invention. In addition, because there are no alumino-hydroxy carbonate minerals in these red muds (because they have not been

precipitated with the addition of the Ca and Mg cations during neutralization), also lack the enhanced pozzolanic attributes of partially neutralized red mud incorporated in cementitious compositions according to the invention. By providing additional pozzolanic qualities and lowered sodium contents compared to un-neutralised red mud, unique and improved qualities are imparted to the compositions of the invention.

Water

Water is important for hydration/activation of the tobermorite gel as well as for lubrication during mixing. The amount of water in the mix greatly affects mix consistency, workability and final strength. Too little or too much water both result in decreased strength. Too little water also results in workability difficulties. For strength, it is preferable to have the mixture slightly too dry than to have the mixture slightly too wet. For shotcrete, it is preferable to have the mixture too wet than too dry and for most grouting applications it is essential to use a wet mix. Water should be added to the dry ingredients and blended until a smooth paste develops. The preferred range of water to be added depends on the partially neutralised red mud blend used, the proportion of acid neutralising hydroxide and oxide minerals present in the blend, the initial water content of the partially neutralised red mud and the intended purpose of the final product.

For load bearing concrete, the preferred range for water addition is from 15% to 55% water to dry ingredients by weight, with a more preferred range of 25% to 45% water to dry ingredients by weight, an even more preferred range of 30% to 40% water to dry ingredients by weight, and a most preferred range of 33% to 37% water to dry ingredients, by weight.

For shotcrete, the preferred range for water addition is from 25% to 80% water to dry ingredients by weight, with a more preferred range of 35% to 75% water to dry ingredients by weight, an even more preferred range of 45% to 70% water to dry ingredients by weight, and a most preferred range of 50% to 60% water to dry ingredients, by weight.

For grout, the preferred range for water addition will depend on the equipment to be used, the porosity and permeability characteristics of the rock or soil material to be grouted and other technical factors, but in general it is from 25% to 98% water to dry ingredients by weight, with a more preferred range of 35% to 95% water to dry ingredients by weight, an even more preferred range of 45% to 90% water to dry

ingredients by weight, and a most preferred range of 55% to 85% water to dry ingredients, by weight. More permeable receiving materials, larger pore sizes, lower pumping distances and larger injection pipe diameters require drier mixtures, whereas lower permeability receiving materials, small pores, long pumping distances and smaller injection pipe diameters favour wetter mixtures.

Silica Providers

Additional silica sources may be included in the mix, to enhance tobermorite gel formation. These may include silica sand, diatomaceous earth, fly ash, bottom ash or crushed silicate rock. The additional silica source may be added either singly or as a combination. The preferred concentration of the added silica source is in the range of 0% to 30% by dry weight, a more preferred range is from 3% to 20% by dry weight, and a most preferred range is from 5% to 12% by dry weight.

Plasticisers/polymerisers

Plasticisers/polymerisers may also be added to the mix to provide greater workability of the wetted mixture, to inhibit initial setting time and to provide additional binding strength to the cured product. Plasticisers/polymerisers include, but are not limited to, Methocell®, cellulose ethers, methyl-hydroxyethyl-cellulose (MHEC), hydroxypropyl-methyl-cellulose (HPMC) and Bricky's Mate™. Highly substituted organic plasticisers/polymerisers are preferred for the addition to mixtures using partially neutralised red mud blends (eg HPMC). In low ionic strength systems (eg freshwater rinsed partially neutralised red mud) less highly substituted plasticisers/polymerisers may be used (eg MHEC). A preferred concentration of added plasticiser is in the range of 0% to 8% by weight of the dry mixture, a more preferred concentration is in the range of 0.1% to 5% by weight of the dry mixture, an even more preferred concentration is in the range of 0.2% to 3% by weight of the dry mixture, and a most preferred concentration is in the range of 0.3% to 2.0% by weight of the dry mixture.

Air Entraining Agents

The entrainment of air provides increased porosity and permeability within the final product. Air entraining agent's work by increasing the trapping ability of air sheared into the concrete during mixing or through the release of gases under the chemical conditions of the slurry, during mixing and setting. The use of air entraining agents increases the

concrete's ability to expand and contract, without cracking, and hence protects the final concrete product against repeated freeze and thaw action in cold climates.

Air entraining agents include, but are not limited to, hydrogen peroxide, organic polymers and commercially available organic foaming agents (eg EP2021™). Hydrogen peroxide breaks down under the chemical conditions of the slurry. It releases oxygen that expands to provide porosity. The migration of gas bubbles provides pellet permeability via interconnected porosity. Air entraining agents are not affected by the vibro-compaction of the slurry during moulding.

Hydrogen peroxide may be used as an air entraining agent, in varying strengths. The strength is preferably in the range of 0.1% to 75% weight to volume hydrogen peroxide, more preferably between 1% to 30% weight to volume, and most preferably between 3% to 10% weight to volume. For a 3% weight to volume strength, addition rates are preferably between 1 mL and 25 mL per kg of dry mixture, more preferably between about 2 mL and about 20 mL per kg of dry mixture, even more preferably between about 5 mL and about 15 mL per kg of dry mixture, and most preferably between about 8 mL and about 10 mL per kg of dry mixture. Higher addition rates or higher concentrations of the air-entraining agent provide greater porosity and permeability, but lower physical strength.

Phosphatising Agents

The development of apatite like minerals and/or phosphate cross-linking between mineral crystals may provide additional strength benefits, especially wet strength. Phosphate may also act to trap and bind heavy metals. Phosphatising agents may therefore be added to the mixture and may include phosphoric acid, tri-sodium phosphate, di-sodium hydrogen-phosphate, sodium di-hydrogen phosphate, tri-potassium phosphate, di-potassium hydrogen-phosphate, and potassium di-hydrogen phosphate. Phosphoric acid with a preferred strength between 0.01 M to 18 M may be used, more preferably a phosphoric acid strength of 0.1 M to 5 M may be used, and even more preferably a phosphoric acid strength of 0.5 M to 3 M may be used. A most preferred phosphoric acid strength is 1 M to 2 M. At a phosphoric acid strength of 1.5 M, an addition rate of 0.2 mL to 4 mL per kg of dry ingredients may be used, a more preferred addition rate is 1 mL to 3.5 mL per kg of dry ingredients, a still more preferred addition rate is 1.5 mL to 2.5

mL per kg of dry ingredients, and a most preferred rate is 2 mL to 2.5 mL per kg of dry ingredients.

Organic Matter

The incorporation of organic matter during formation of a cementitious composition
5 can provide a fibrous mat, while the xylem and phloem of the tissue can provide
additional interconnecting pathways for fluid flow. In addition, organic matter may
provide a suitable bacteria growth medium. The formed products may be used in
anaerobic treatments, of efficient, and may allow biogeochemical reactions (eg sulfate
reduction, and denitrification) to progress efficiently. Organic matter that may be
10 incorporated into the product include, but is not limited to, sewage biosolids, sugarcane
bagasse, straw chaff, mulch, and hemp fibres. The concentration of added organic matter
may be in the range of from 0% to 15% by weight of the dry mixture. A preferred
concentration is in the range of 0.4% to 10% by weight of the dry mixture, an even more
preferred concentration is in the range of 0.6% to 8% by weight of the dry mixture, and a
15 most preferred concentration is in the range of 0.8% to 5.0% by weight of the dry
mixture.

Reinforcing

Reinforcing of large structures and concrete pours may be necessary where the
concrete will be load bearing, especially under tensile stress. Most typically, reinforcing
20 of concrete is achieved using steel reinforcing. However, chloride ingress and steel
corrosion often leads to a breakage of the concrete, because of corrosion swelling around
the reinforcing rods. Consequently, conventional reinforcing steel is often galvanised, or
epoxy coated to isolate the steel from the corroding salt. Alternatives to this are the use of
cathodic protection by inducing a current so that the steel is cathodic. Another alternative
25 is to use corrosion resistant steels (e.g. stainless steel), or non-steel alternatives such as
glass fibre, aramid fibre, carbon fibre, polypropylene fibre or polyethylene fibre. Fibres
may be added to the concrete as short fibres (approximately 50mm length) to provide a
cross-linked mat for the concrete to set around and to provide improved strength.

Set accelerants

30 A set accelerant may be added to the cementitious composition according to the
invention to provide rapid setting, by promoting the formation of C3A, C4AF
components in the composition or by inducing other high water demand mineral growth.

However, the initial acceleration of the setting process of a cementitious composition often has a trade off, in that the final strength thereof may be reduced. Set accelerants are typically, but not always, inorganic in nature and may provide compounds that are utilised in the early stages of setting, or that produce water-demanding products. Set accelerants include, on the inorganic side, alkali metal (K, Na & Li) hydroxides, oxides, aluminates and carbonates, alkali-earth metal (Ca & Mg) hydroxides, oxides, aluminates, or carbonates, fumed silica, silicic acid, ferric salts (including chloride, nitrate and sulfate), and montmorillonite clays, or, on the organic side, N, N-dimethylacrylamide, AMIS, RMT, naphthalenesulfonic acid and formaldehyde.

10 Set retardants

A set retardant may be added to slow down the initial setting of the cementitious composition. A common set retardant is gypsum (calcium sulfate dihydrate). It may have been added to the hydraulic cement specifically for this purpose. By retarding the set time of the concrete, it allows for a much longer working time for smoothing, working, and pouring of the concrete. This is especially important when a single continuous large pour is required. In addition, by slowing the setting process down, there is less likelihood of cracking and shrinkage of the concrete. Gypsum may be used in combination with tri-ethanolamine, to prevent shrinkage.

Salt Resisting Agents

20 Salt resisting agents aid in protecting the set product against saline waters. Concretes with a low C3A content are more resistant to sulfate attack. By including an additive that shifts the setting structure away from C3A to C4AF, C2S, C3S and other compounds such as CA, C3A4 (tri-calcium tetra-aluminate), and C2AS (di-calcium alumino-silicate) greater salt protection can be obtained. In order to achieve greater salt resistance, ferric salt or calcium aluminate may be added to the composition. Some plasticisers could be affected by the salinity of the mix water, decreasing their performance. For example, MHEC (methyl-hydroxy-ethyl cellulose has a low salt tolerance and the strength provided in low salt environments is lost when mixed in a high salt environment. However, this can be overcome by using a high salt tolerant variant
30 HPMC (hydroxy-propyl methylcellulose).

Other additives

Other components may be added to the mix, as desired, to change the geochemical and physical characteristics of the final product and may include, but are not to be limited to, silica providers, plasticisers, phosphatising agents and air entraining agents.

Mixing of ingredients

Dry materials may be sieved, preferably to < 2 mm, more preferably to < 1 mm, even more preferably to < 500 μm and most preferably to < 250 μm . They are preferably fully mixed to reduce material clumping. Wet materials (water, any phosphatising agent, and any air entraining agent) are preferably mixed together before addition to the dry materials. They may alternatively be added individually. If the wet ingredients are to be individually mixed with the dry ingredients then the mixing order may be water before the phosphatising agent, before the air entraining agent. Extended mixing of the slurry (i.e., going from a slightly wet to slightly dry slurry) may be performed, to ensure complete entrainment of air during the mixing process as air entrainment is substantially reduced once mixing is stopped. The phosphatising agent may be phosphoric acid. The air entraining agent may be hydrogen peroxide.

Mixing can be achieved by a number of means, including by commercially available shear-force mixers, and concrete mixers that turn over the materials. When the materials are mixed, mixture is preferably folded in on itself for at least 5 minutes, preferably for at least 10 minutes, at a rate of at least 10 times per minute, preferably at a rate of at least 20 times per minute, and more preferably at a rate of at least 30 times per minute. (These rates may be the same as the revolutions per minute for commercially available concrete mixers). A shear-force mixer (such as a bread mixer) may be used at higher mixing rates than standard concrete mixers. Depending on the machine specifications, mixing times may be adjusted accordingly.

Pouring, Moulding and Drying

Optimum concrete strength is usually attained after curing for about 28 days. However, curing will continue for many months and even years. Initial setting of cement is achieved by the development of the C3A1 and C4A1F forms of tobermorite, over a period of 0-10 days. The C3S and C2S tobermorite gel usually forms over a period of 0-400 days.

To maximise strength, the poured product is preferably maintained in an environment that restricts moisture loss, for a period of at least 28 days before use. During curing, temperatures are preferably kept as cool as practicable, to minimise loss of water, and to promote C3S tobermorite development. The product is preferably allowed
5 to cure for at least 28 days to provide for the development of a C3S tobermorite gel, to form a product that has a low quantity of fines (< 0.15 mm) and a low potential for creating a dust problem.

Hebel Concrete

Hebel concrete is a highly porous, lightweight concrete which is used for weight
10 saving in non-load bearing wall constructions. Typically, it is moulded into blocks, but it can be poured into large slabs and lifted into position. The method of manufacture is the same as for a typical concrete except that a foaming (extreme air entraining) agent such as EP2021, is added. Upon mixing, EP2021 foams much like shaving cream to provide a
15 very porous cement composition that sets while preserving the porosity. Because of its porosity, Hebel concrete has a high capacity to store water therefore is ideal for concrete planter boxes and the like.

Shotcretes

A shotcrete that can be sprayed onto walls and ceilings may be prepared by the process in accordance with the invention. To accomplish this, a super-plasticizer may be
20 added to a composition according to the invention, in order to improve the pumpability of the ultimate shotcrete composition, when it is prepared for use by adding water to cause the formation of a tobermorite gel that will adhere to a vertical wall when sprayed thereon. The hydrated mixture, which preferably contains no more water than is necessary to facilitate efficient pumping of the mixture, is then pumped and sprayed on to the
25 vertical wall, through a spray nozzle. Just prior to emerging from the spray nozzle, a set accelerant is added to the already hydrated composition. For some applications, fibre reinforcing may also be added at this point. The set accelerant causes rapid setting of the sprayed concrete before it can slump from the wall. Typically, the set accelerant is a dry powder such as fumed silica, an alkaline earth or an alkaline metal hydroxide.

Grouts

Grouts to be used in environmental applications such as sealing leaks in rock or soil material near dams or other structures where it is necessary to keep water either in or out.

The compositions according to this invention are particularly useful where the fluids to be controlled by the grouting process are acidic, caustic, saline, acidic and saline, or caustic and saline. The exact grout mixture required will depend on the geotechnical properties of the rock or soil to receive the grout, the equipment to be used to emplace the grout and the composition of the water to be controlled by the grouting process. Workability and setting characteristics are particularly important in determining grout composition, but strength is less critical because most of the strength requirements will be met by the rock or soil material being grouted and any additional strength resulting from grout emplacement will usually be comparatively small.

Examples

Example 1: Cementitious Compositions according to the invention.

Table 2					
Sand	Gravel	Cement	Other*	Partially neutralised Red Mud	Purpose
0-1	0	1	0-2	2-5	Constructive Concrete
1-2	0-1	1-2	0-3	6-8	Acid Resistant Concrete
1-2	0	1	0	1	Paver

*other components include but are not limited to fly ash, silica fume, plasticizer, phosphoric acid, air entraining agents and reinforcing fibres.

Example 2: Further Cementitious Compositions according to the invention.

Table 3					
Sand	Gravel	Cement	Other*	Partially neutralised Red Mud	Purpose
0-15	0-5	1-15	0-10	1-50	Specialist Shotcrete
0-10	0-5	1-20	0-5	1-30	Hebel Concrete
1-4	1-4	1-3	0-2	1-3	Construction Concrete

*other components include but are not limited to fly ash, silica fume, plasticizer, phosphoric acid, air entraining agents and reinforcing fibres.

Example 3: Partially neutralised red mud as a Pozzolan (cement replacement) in cementitious paste.

Four paste mixtures, respectively designated A, B, C and D, were prepared. Mixture A was prepared according to Australian Standard AS 1315. Mixtures B, C and D were prepared in a similar manner, except that instead of using 100% Ordinary Portland cement (OPC), these mixtures were prepared by mixing ordinary Portland cement (OPC) with increasing percentages of a slurry of partially neutralised red mud, of which the pH had been reduced to between 8.2 and 10.5 by reacting red mud with an aqueous solution having a hardness supplied by calcium plus magnesium of greater than 5 millimoles calcium carbonate equivalent. The slurry contained approximately 51% solids.

The amounts of OPC replaced with partially neutralized red mud were as listed in Table 4. The percentages replaced were respectively 5%, 10% and 20%. All four mixtures were 25 mm cubes, and all four mixtures were cast at a water to binder ratio of 0.45.

All four mixtures were allowed to cure continuously in sealed plastic bags stored in a fog room at 23°C for 56 days and samples of each were then tested for compressive strength. The results were as follows:

Table 4				
Mixture	% partially neutralized red mud	Flow (mm)	Initial setting time (minutes)	Compressive stress after 56 days (MPa)
A	0	220	275	82
B	5	220	325	73
C	10	205	305	73
D	20	150	320	62

The final setting times were between 300 and 340 minutes with no discernable difference between the various mixtures.

In the case of mixture A (100% OPC), the compressive strength of the cured paste was 70 MPa after 28 days, whereas in the case of mixture D (20% replacement of OPC with partially neutralized red mud), the compressive strength of the cured paste, after 28 days, was 60 MPa.

The semi-adiabatic temperature of the cured paste (after 28 days) in the case of 100% OPC was 42°C, whereas the semi-adiabatic temperature of the cured paste (after 28 days) in the case of a 20% replacement of OPC with partially neutralized red mud, was 48°C.

5 The flow or slump of each of the mixtures was measured five minutes after mixing. The pastes of mixtures A, B and C were very fluid. However, the paste of mixture D (20% partially neutralized red mud replacement of OPC) was considerably less.

Workability describes the ease with which a paste or concrete can be mixed and placed to give a uniform material. There is no single measure of the property and in this example a modified flow test was used in terms of which the material was compacted into a conical container which was then lifted on one side and the resulting flow of the material was measured. The higher flow indicated a more fluid paste.

10 Setting times for the pastes were determined according to Australian Standard AS 1315. The addition of partially neutralized red mud resulted in an increase in initial setting times for mixtures B, C and D of 18%, 10%, and 17% respectively. This was considered to be an insignificant variation, when compared to the 100% OPC control mixture A.

The final setting times of the mixtures were between 300-340 minutes with no discernible difference between the reference and test formulations.

20 The initial and final setting time measurements of pastes represent specified resistances to the penetration of a needle. There are several variables influencing the penetration of the needle and in this example all parameters were kept constant except for the content of the partially neutralized red mud in the hydrating paste.

Mixtures A, B and C displayed continuous strength development up to 56 days curing, whilst mixture D (20% partially neutralized red mud, 80% OPC) appeared to achieve marginal strength gain after an initial period of 7 days of fog cure.

Example 4: Partially neutralised red mud as a Pozzolan (cement replacement) in concrete.

30 Two mixtures of cementitious compositions intended for use as general purpose concrete having a nominal compressive strength of 40 MPa, were prepared. They were respectively designated mixtures E and F. In mixture E, 100% ordinary Portland cement (OPC) was used as binder. The composition of mixture F was based on a conclusion made on the basis of the results of Example 3, namely, that up to 20% of OPC can be

replaced by partially neutralised red mud to produce a 40 MPa concrete of which the compressive strength is not reduced to below a minimum acceptable level.

Both concretes were mixed to give a slump of 75 mm. It was found necessary to increase the water to binder ratio for the concrete containing the 20% partially neutralized red mud. The compositions of the two mixtures were as given in Table 2, in which the masses of solids are reflected as Saturated Surface Dry weights per cubic meter.

Table 5		
	MIXTURE E	MIXTURE F
Ordinary Portland Cement (OPC) (kg)	325	255.2
Partially neutralized red mud	0	63.8
Water (l)	172	194
Aggregate (14 mm) (kg)	578	567
Aggregate (9 mm) (kg)	652	639
Sand (kg)	790	774
Water reducing agent (l)	1.72	1.69
Water binder ratio	0.53	0.61

Samples of both mixtures were allowed to cure continuously in sealed plastic bags, stored in a fog room at 23°C. Samples were tested for compressive strength after various stages. The results were as follows:

The early age compressive strength development over 3 days, for mixtures E and F, was similar. Between 3 and 7 days' curing, the strength of mixture E increased at a higher rate than that of mixture F. From 7 to 28 days both concretes exhibited similar strength gain, with mixture F having an approx 10% lower strength than mixture E after 28 days fog curing. The reduced 28 day compressive strength of mixture F was attributed to the higher water to binder ratio required for a 75 mm slump as compared to the reference mixture E concrete. This need for a higher water to binder ratio, see Table 6, for an equivalent slump, could possibly be overcome by using a more appropriate water reducing agent.

The differential in water to binder ratio between mixture E and mixture F is believed to be partly responsible for the observed reduced 28 day compressive strength

for mixture F concrete. However both concretes reached their 28 day design strength of 40 MPa.

The peak semi-adiabatic temperatures of both mixtures E and F were around 30.5°C and, in both cases, this occurred after 11.25 hours after commencement of mixing.

The workability of the mixture F was lower than that of mixture E because the partially neutralised red mud acted as a set accelerant. However, the reduction in workability of the mixture was overcome by the addition of a plasticizer. The use of partially neutralised red mud as an OPC replacement provided greater initial strength (7-day curing) and a higher semi-adiabatic temperature, after 7 days curing, of 31.5°C. The aforementioned increase in semi-adiabatic temperature is of importance where a low surface area to volume ratio is present, because it may lead to early age cracking from thermal stress. The increase in semi-adiabatic temperature may have been caused by a greater proportion of tetra-calcium alumino-ferrite (C4AF) that was produced during curing and because less tri-calcium silicate (C3S) and di-calcium silicate (C2S) were formed in the Portland cement used in the concrete. Alternatively, the cement may have been converted into a high alumina type cement, because of the additional aluminates supplied by the partially neutralised red mud.

Example 5: Fine Detail Preservation.

Three nonporous compositions (4 parts partially neutralised red mud and 1 part cement; mix G), (3 parts partially neutralised red mud, 1 part sand and 1 part cement; mix H), and mortar (4 parts sand and 1 part cement; mix I), were poured into 250 mL moulds, where fine embossed lettering for volume graduations was present on the inside wall of the mould. When the blocks had cured the moulds were broken away and both mixes G and H had preserved the fine detail such that the graduations were easily read, whereas mix I had not preserved this detail. The preservation of fine detail on the surface of a cementitious composition is important for the production of non-slip tiles and concrete paths. The fine detail able to be taken by the partially neutralised red mud in cementitious compositions suggests that fine detail can be created on the surface of tiles or other fabrications such as concrete sculptures or decorative (e.g. embossed or moulded) facings for buildings and walls. Very fine lines that can use the capillary draw provided by surface tension of water may draw water into these fine channels and remove the water before it becomes a slip hazard.

Example 6: Terracotta tiles

A porous styled cement composition comprising 1 part cement, 1 part sand and 3 parts partially neutralised red mud was produced that had very good wetting and drying resistance. Terracotta cement pavers made from this composition also had a good freeze/thaw resistance. These pavers compared favourably with conventional pavers made by sprinkling an oxide powder on the surface of cement pavers, after they have been formed and whilst the pavers were still wet. In the case of such conventional pavers, wear on the oxide coating after some time reveals the underlying (uncoloured) cement, whereas wear on tiles made according to the processes of this invention has no impact on colour because the tiles have a uniform colour throughout.

Example 7: Blown cement compositions

By combining the composition of Example 5 with EP2021 (a foaming agent), lightweight (porous) flagging stones and tiles were produced.

Example 8: Acid Neutralisation.

Three nonporous compositions, mix J, mix K, and mix L, were prepared as in Example 3. One sample from each mix was allowed to cure for several days before drilling a central hole into it and sawing off a 1.5 cm thick slab. The three slabs were then suspended in separate 1 L jars of milli-Q water and the pH was adjusted to 2.5. The pH of each was readjusted every few days back to pH 2.5 with small additions of sulfuric acid until a total of 50 mL of sulfuric acid had been added to each jar. After the incremental addition of 50 mL of the acid to each jar over about 2 months, the samples were allowed to equilibrate with the solution in the jar for 4 weeks to bring the solution pH into equilibrium with the slabs, before they were removed to allow examination of the surfaces. Solution pH during the 4 week equilibration time was monitored twice weekly. Sample J reached equilibrium with the cement slab within the first week, sample K reached equilibrium by the middle of the second week, and sample L reached equilibrium by the middle of the third week. The final equilibrium pH of each of the solutions was as follows:

For the sample of mix J:	7.94;
For the sample of mix K:	7.88;
For the sample of mix L:	7.79.

The mix J and K cements raised the pH in the acid solutions much faster than the sample of mix L, indicating that the acid neutralising capacity of the sample of each of these mixtures was more readily available. The sample of mix L finished with quite severe surface etching of the slab and surface mineral deposition. Both the samples of the mix J and K cements showed some etching, but not as much as the sample of mix L. Both the samples of the mix J and K cements also showed mineral deposits on their surfaces, with mix J having the greater amount of deposit. The sample of the mix K cement had fine acicular mineral crystals on its surface.

Example 9: Acid resistance.

One sample of each of mixtures E and F (of Example 4) was immersed in 10% acid solutions of each of HCl, HNO₃, and H₂SO₄. After 8 weeks, all the samples were removed and the mass loss of each was measured. After 1 week in each of the acids, the Portland cement control (mixture E) had completely disintegrated, with a 100% loss, whereas the sample of mixture F immersed in the 10% HNO₃ had lost only 10% of its mass, the sample of mixture F immersed in the 10% HCl had lost about 20% of its mass, and the sample of mixture F immersed in the 10% H₂SO₄ had lost about 40% of its mass.

At 10% strength, the molarities of the acids were 1.2 M for HCl, 1.6 M for HNO₃ and 1.8 M for H₂SO₄. The moles of H⁺ available for attack on the composition were the same for the HCl and the HNO₃, but for the H₂SO₄, there were 3.6 M available. It was thought likely that the greater loss of material from the sample immersed in the sulfuric acid was caused by the 3 times greater hydrogen ion availability compared to that for the HNO₃. The greater susceptibility of the mixture containing partially neutralised red mud to attack by HCl may be explained by the lower resistance to chloride of the compositions according to the invention.

Thus, cementitious compositions prepared in accordance with the invention are particularly suitable for use in areas affected by acid sulfate soils or oxidising sulfidic waste rock or tailings at mine sites. Sulfate resistance is normally associated with a reduction in the proportion of tri-calcium aluminate (C3A) component, and for sulfate resistant cement, a C3A content of 4-10% is desired. The sulfate resistance of compositions according to the invention coupled with the ability to shotcrete the slurry, provide a material that can be sprayed onto open cut pit walls to minimise acid leaching and to prevent oxygen diffusion, preventing further sulfide oxidation.

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